SURFACE WATER CONTAMINATION BY LANDFILL LEACHATES

RMD Report L-90

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SURFACE WATER CONTAMINATION BY LANDFILL LEACHATES

by

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for

RESEARCH MANAGEMENT DIVISION
Alberta Environment

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EXECUTIVE SUMMARY

This study was carried out at the Kananaskis Centre for Environmental Research in Calgary, Alberta. It was designed to assess the toxic effect of leachates from the Clover Bar Landfill on waters of the North Saskatchewan River. Samples from three(3) different locations (including the river) were taken and analyzed utilizing the Beckmann Microtox procedure. Selected samples, where low toxicity might be encountered, were assessed by the freeze concentration method in order to enhance detection.

Total organic carbon analyses indicated that the strength of the leachates had decreased significantly over the past three years. Toxicity measurements as a result of the freeze concentration procedure revealed nothing as a result of organic bases, slight levels due to organic acids, random slight measurements due to phenols, and major levels due to neutral organic compounds.

Based on these observations, leachates from the old part of the Clover Bar Landfill have probably decreased over the past several years to the point that the site would not create a situation requiring additional monitoring or remedial action.

TABLE OF CONTENTS

		Page
LIST OF TABLES		x
LIST OF FIGURES		xi
ABSTRACT		xii
ACKNOWLEDGEMENTS		xiii
1.	INTRODUCTION	1
2.	STUDY AREA	4
3.	MATERIALS AND METHODS	5
3.1	Samples	5
3.2	Carbon Analyses	5
3.3	Microtox Analysis	7
3.4	Test Procedure	8
3.5	Freeze Concentration of Leachate Samples	9
3.6	Ion Exchange for Fraction Separation	10
3.7	Samples Requiring Concentration before Fraction Separation	11
4.	RESULTS AND DISCUSSION	12
5.	SUMMARY AND CONCLUSIONS	25
6.	REFERENCES CITED	27

LIST OF TABLES

		Page
1.	Organic Constituents of Clover Bar Leachates, 1981.....	13
2.	Organic Carbon in Leachate and River Samples, 1984.....	14
3.	Microtox EC_{50} (5), EC_{50} (15), and Equivalent Toxic Units of Leachate and River Samples, 1984.....	16
4.	Freeze Concentration Effect on TOC Values.....	18
5.	Microtox EC_{50} (5), EC_{50} (15), and Equivalent Toxic Units of Separated Fractions of Samples.....	20
6.	Toxicity Material Balances.....	23

LIST OF FIGURES

Page

1. Sample Well Locations in the Clover Bar Landfill Site..... 6

ABSTRACT

This study was carried out at the Kananaskis Centre for Environmental Research and was initiated as a result of an unsolicited proposal submitted to the Alberta Government.

The Clover Bar landfill is operated by the City of Edmonton and has been constructed to avoid contamination of the adjacent North Saskatchewan River. The design included provisions for the diversion of ground water around the landfill operation and impervious dykes lined with compacted clay in order to isolate the landfill from the river.

The toxic effect of Clover Bar landfill leachates on waters of the North Saskatchewan River was assessed using the Beckman Microtox procedure. A total of eight samples were taken: three from wells within the main landfill site; three from wells between the landfill and the river; and two from the river, one upstream and the other downstream of the landfill. Total organic carbon (TOC) analyses indicated that the strength of the leachate has decreased significantly in the past three years. Initial Microtox measurements showed relatively low toxicities in all well samples, no detectable toxicity levels in the upstream river sample, and minor toxicity in the downstream river sample.

A procedure of freeze concentration was applied to enhance levels of toxicity in selected samples where, following fractionation into different classes of organic compounds, low levels of toxicity might be encountered. Fractionation of whole samples into the four major classes of compounds was accomplished using ion exchange techniques. Toxicity measurements of the fractions revealed none due to organic bases, slight levels due to organic acids, random slight measurements due to phenols, and major levels due to neutral organic compounds.

Based on these observations, leachates from the old part of the Clover Bar landfill have probably decreased over the past several years to the point that the site would not create a situation requiring additional monitoring or remedial action.

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1. INTRODUCTION

Sanitary landfills, the most common waste disposal method used in the industrial world, present potentially serious environmental problems through the movement of hazardous material from the landfill site into groundwaters and surface waters. The problem is potentially more serious at sites where hazardous waste materials are emplaced in addition to regular municipal and industrial wastes. The Clover Bar sanitary landfill in Edmonton is one such site.

Potential problems arise in sanitary landfill sites due to processes that form a liquid accumulation called leachate. Leachate generation occurs as a result of two concomitant processes that alter the character of the deposited waste material: snow and rain water percolation through the waste material and degradation of organic substances in the waste by microbial action (Baedecker and Back 1979; Chen and Bowerman 1974; Livermore et al. 1969; Oleckno 1976; van Engers 1978). Leachate formation depends on factors such as type of waste material deposited, landfill conditions (temperature, pH, Eh, moisture, and age), characteristics of external water, and composition of the covering soils (Baedecker and Back 1979). Groundwater is also a contributor to the leachate entity. Leachates differ from one landfill site to another, depending on the operating conditions of the landfill. In sites where hazardous and liquid wastes are deposited, the character of the leachate is altered (Oleckno 1976). When leachate forms in sufficient quantity to migrate beyond the boundaries of the landfill site into groundwater aquifers or surface waters, it can pose a threat to human health and other living systems.

To address these situations adequately, one must become familiar with present procedures of landfill operations, characterization of leachates and other hazardous substances in landfills, processes that occur in landfills, and possible changes in each of these aspects of waste management that could be implemented. One specific concern of waste management that must be addressed is the nature of the leachates generated in the landfills.

Alberta is growing rapidly, both in population and in industry. This growth brings with it new technologies that are used in all aspects of our lives. Concomitantly, it also generates new kinds of wastes that must be handled by the municipal and industrial authorities. In most cases these wastes are deposited in sanitary landfills such as the Clover Bar Landfill. Many of these waste materials are both hazardous and non-biodegradable, therefore it is likely that with time these could create problems in the areas where they are located.

In a recent study by Reinhard, Goodman, and Barker (1984), leachate plumes from two sites in Ontario (Waterloo and North Bay) were characterized with respect to trace organic compounds. The presence of aliphatic and aromatic acids, phenols, resin acids, and terpene compounds made up the main components of the plume, accompanied by compounds probably related to industrial activity. These included chlorinated benzenes, aromatic hydrocarbons, alkyl phosphates, and alkylphenol ethoxylates. The authors suggested that most of the compounds were persistent and mobile in the methanogenic plume. They also studied leachates escaping from a sanitary landfill with no impervious liner to determine the effect on water quality in groundwater aquifers.

The Franklin County Landfill in Indiana is located in an abandoned gravel pit and apparently has no negative effect on local groundwaters. This has been attributed to dilution of the leachate by flowing groundwaters (Sullivan and Morgan 1982).

The objectives of the present study were threefold: to measure the toxicity of sanitary landfill leachates using a bacterial luminescence assay; to measure the toxicity of adjacent river water using the same assay; and to determine the classes of compounds responsible for the majority of the toxicity in both sets of samples. The study was carried out in the Clover Bar Landfill in North Edmonton, Alberta. This landfill is located in an abandoned gravel pit through which groundwaters pass readily, and also where the North Saskatchewan River flows along the north side of the site. In such situations, the probability for contaminating both surface water and groundwater is high. The results of this study will indicate directly the

potential hazard existing between leachates generated in the landfill and the water quality of the adjacent river.

The present research provides information on one aspect of organic characterization of Alberta landfill leachates. It also provides a measure of the integrity of one sanitary landfill insofar as leachate escaping from the site is concerned.

2. STUDY AREA

The Clover Bar site is located in Section 28, Township 53, Range 23 West of the 4th Meridian, just east of the city of Edmonton, and is situated on a river terrace on the south bank of the North Saskatchewan River. In this area, alluvial deposits reach a thickness of 8 m with a lower layer of gravel. The gravel layer contains a substantial amount of groundwater, which moves along the surface of the underlying bedrock and appears as springs at the river (Wardrop and Associates 1978). This landfill has a clay liner in addition to a groundwater interceptor and a leachate collection system. The landfill site intercepts the gravel layer. Waste material deposited in the site is principally municipal, with some industrial and hazardous wastes. Potentially hazardous liquid wastes make up about 3% of the total amount deposited (Wardrop and Associates 1978).

3. MATERIALS AND METHODS

3.1 SAMPLES

Eight samples were studied in this project. Three of these were from the main landfill area and represented the oldest to the most recent locations; three were from outside the berm between the landfill and the North Saskatchewan River; and the last two were river water samples, one taken at a short distance upstream of the landfill and the other at a similar distance downstream. The landfill leachates were obtained from wells drilled by Alberta Environment several years ago. Attempts were made to sample all wells inside the main landfill; however, with the exception of those actually studied, no leachate was available from any of the others for study. All samples were collected by Alberta Environment personnel using bailers. The samples were then stored in acid-washed glass bottles with Teflon-lined caps. They were placed in ice chests for transportation to the laboratory, where they were stored in a refrigerator at $4^{o}C$. The sample locations in the landfill site are illustrated in Figure 1.

3.2 CARBON ANALYSES

Total organic carbon (TOC) analyses were conducted on all samples studied using a Dohrmann DC-80 Analyser. This instrument is capable of measuring total carbon, volatile carbon, organic carbon, and inorganic carbon by difference. Total carbon is determined by direct injection of an aqueous sample of appropriate size into the analyser. Three options for sample size are available depending on the concentration of carbon in the sample: 40 L for samples with a concentration above 2000 mg/L; 200 L for concentrations of 500 mg/L; and 1.0 L for concentrations less than 20 mg/L. Standard solutions of potassium acid phthalate are prepared for each range. Volatile carbon is determined by sparging the sample with oxygen for 10 min prior to analysis using the sparging apparatus that is part of the DC-80 Analyser. Similarly, organic carbon determinations are obtained by adding a couple of drops of a 10% nitric acid solution and sparging for 10 min prior to injection. The total organic carbon is obtained by adding the result to that of the volatile carbon reading.

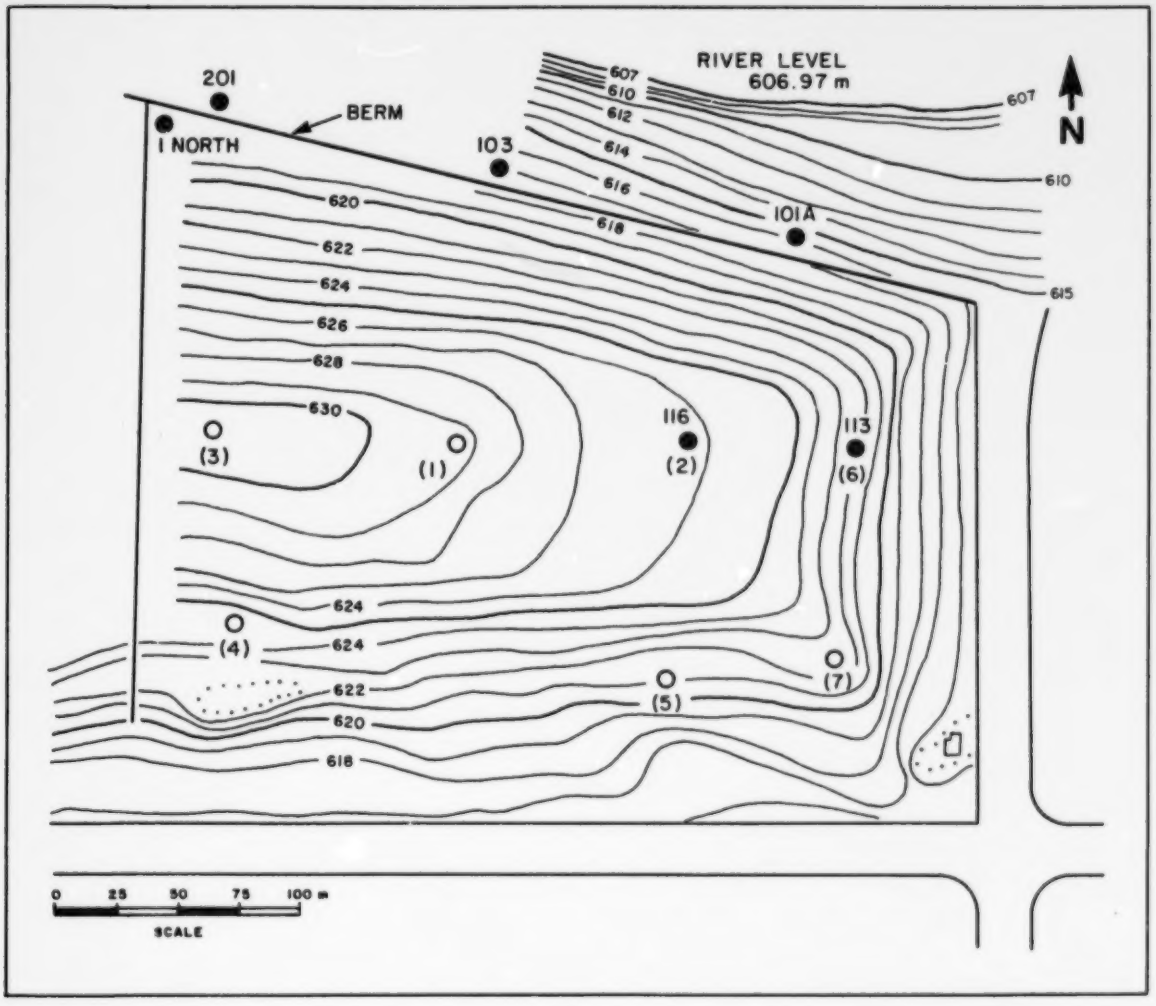

FIGURE 1. SAMPLE WELL LOCATIONS IN THE CLOVER BAR LANDFILL SITE.

Total inorganic carbon is determined by subtracting total organic carbon from total carbon.

3.3 MICROTOX ANALYSIS

The method used to determine the toxicity of the landfill leachate samples is one developed by Beckmann Instruments based on observations made by Robert Boyle in 1672. Boyle published his observations of meat sections that were colonized by luminescent bacteria (Beckmann Instruments 1982). Although at the time he was unaware of the biological nature of the "shining flesh," he did discover its susceptibility to the effects of harmful chemicals such as ethanol, turpentine, hydrochloric acid, and ammonia. These toxicants caused a rapid decrease in the light output of the organisms, while rinsing with water had no such effect.

Since that time, many studies have been conducted using luminescent bacteria under controlled conditions in an effort to carry out toxicity measurements. The Microtox system uses a suspension of marine luminescent bacteria in which the organisms are "challenged" by the addition of several concentrations of an unknown sample. The Microtox Analyser measures the light output of the organisms before and after they are challenged. A reduction of light indicates a deterioration in the state of health of the organisms and signifies the presence of toxicants in the sample. The Microtox system determines the mean toxic response of approximately one million bioluminescent organisms. The use of such a large population enables the results from Microtox analyses to have very high resolution and statistical significance when compared with those obtained using relatively small populations in fish and invertebrate bioassays for economic reasons. Comparison studies have proved that Microtox system results compare favourably with those produced by the traditional 96-h fish bioassay, and can usually be obtained in much less time. The Microtox Reagent, which consists of lyophilized bacteria, can be handled conveniently as an ordinary chemical reagent (Beckmann Instruments 1982).

The Microtox system is very flexible, and has many areas of application, which include monitoring the toxicity of industrial effluents, determining the potential hazard of new chemicals, controlling waste

treatment and other processes involving reactive compounds, studying synergism and antagonism of toxic mixtures, and monitoring the fate of toxic substances in the environment.

The expression that describes the toxicity as measured in the Microtox system is the effective concentration (EC) of the sample that causes a specific effect. Usually the expression is the EC_{50}, which means the effective concentration causing a 50% decrease in the light output of the Microtox Reagent. This expression usually includes two other terms for a more specific definition: EC_{50} (t, T), where t is the time of exposure and T is the temperature in degrees Celsius at which the test was conducted. An EC_{50} of 100% indicates that at full sample strength, 50% of the luminescent bacteria will be killed in the time of the test (5 min or 15 min).

The Microtox Reagent is a lyophilized strain of marine luminescent bacteria most closely resembling Photobacterium phosphoreum in its characteristics. This particular strain was selected because of its suitable light output and its sensitivity to a wide variety of toxicants. The freeze-dried reagent must be reconstituted with specially purified water (sold as Microtox Reconstitution Solution) immediately before use. Microtox diluent is also specially purified water containing 2% sodium chloride, and is used to dilute test samples of the reconstituted reagent before testing. It is also used as a reagent blank. Microtox Osmotic Adjusting Solution is specially purified water containing 22% sodium chloride for adjusting the molality of a test sample to 2% sodium chloride. The luminescent bacteria used in this test are marine bacteria that require this strength of salt solution in the test sample. Micropipettes with disposable plastic tips are used to measure all solutions in the Microtox test.

3.4 TEST PROCEDURE

The test procedure used in this study was designed by Strosher (1983). A detailed description of the sample preparation and Microtox TM procedures for sump fluid samples can be obtained from Strosher's (1983) report.

3.5 FREEZE CONCENTRATION OF LEACHATE SAMPLES

The freeze concentration technique involved taking an aliquot of the leachate sample (500 mL), placing it in a round-bottom flask, and attaching the whole to a rotary evaporator. The rotary evaporator provided a mechanism for revolving the flask in a bath containing methanol cooled with dry ice. No vacuum was applied to the rotary evaporation apparatus except what was required to hold the sample-holding flask to the rotary evaporator. The temperature of the bath beneath the flask was maintained near -2°C for at least 45 min with the flask rotating rapidly. The temperature was slowly lowered (about 1°C/15 min) until the first freezing occurred as the formation of slush in the rotating solution. The temperature was then maintained near that at which slush formation occurred until a layer of ice was formed on the inside walls of the sample flask. This ice represented pure water frozen out of the solution. This process permitted concentration of the original sample through freezing out of water. Once a significant layer of ice was formed on the inside walls of the flask, the temperature was lowered once more with dry ice, thereby increasing the rate of freeze-out of water on the walls of the flask.

Slush formation could continue through to the final stages of the freeze concentration. This created no problems unless the slush formation approached proportions large enough to permit organic material to be trapped in the ice on the walls of the flask, thus reducing the efficiency of the freeze-concentration process. At the end of the process, any small remaining amount of slush was removed by permitting the flask to rotate out of the methanol bath in the air, thereby allowing a slight warming to occur. This step had to be carefully watched because too much warming would allow some melting of the ice from the wall, causing some of the concentrated solution to be trapped in the ice. Such an occurrence results in a loss of concentrated solution, reducing the efficiency of the freeze-concentration process.

The efficiency of the concentration was calculated by measuring the TOC of the original sample for both the pure ice and the concentrated sample. the volumes of the melted ice and the concentrated sample were recorded to enable cross-checking between TOC values of the original sample and the

new solutions. It was the comparison of the TOC values and the volume taken of the freeze concentration of the original sample with the TOC of the concentrated sample and its volume that gave the measure of the concentration efficiency that occurred as a result of the freeze-concentration process. For example, assuming that the TOC of the original sample was 10 mg/L and the quantity taken for concentrating was 500 mL, if the final concentrated solution had a volume of 100 mL with a TOC of 50 mg/L and a melted ice volume of 400 mL with a TOC of 1.0 mg/L, the effective concentrating factor would be 5:1 for the organics in the solution. Therefore it could be assumed that the concentrating factor for organic substances contributing to the toxicity of the overall sample also would be concentrated to the same extent.

The freeze-concentration method enabled accurate records to be made for toxic compounds that might have been unmeasurable using the Microtox procedures. This concentrated solution also could be treated to obtain better fractions containing individual classes of organic materials that would contribute to the overall toxicity of the original sample.

3.6 ION EXCHANGE FOR FRACTION SEPARATION

Two ion exchange resins were mixed to create the proper separation of organic substances into the four desired fractions: organic acids, organic bases, phenols, and neutral compounds. Equal amounts of XAD-2 and XAD-8 resins were mixed thoroughly then added to each of several 25 mL burettes to a depth of 10 mL. Each column was generated by flushing through 50 mL of 0.1N hydrochloric acid, 50 mL of pH 7 buffer, 50 mL of 0.1N sodium hydroxide, and 50 mL of methanol sequentially, followed by rinsing with 200 mL of double-distilled water.

Fifty millilitres of test sample was placed in the ion exchange column. The organic bases were eluted with 25 mL of 0.1N hydrochloric acid (for a total volume of 75 mL), organic acids were eluted with 50 mL of pH 7 buffer (for a total volume of 50 mL); phenols were eluted with 50 mL of 0.1N sodium hydroxide; and the neutral compounds were eluted with methanol.

Prior to Microtox assay, the pH of each fraction was adjusted to pH 7 using hydrochloric acid for the sodium hydroxide fraction and sodium

hydroxide for the hydrochloric acid fraction. The methanol fraction was evaporated to complete dryness, then it was taken up in double-distilled water.

3.7 SAMPLES REQUIRING CONCENTRATION BEFORE FRACTION SEPARATION

Initial Microtox assessments indicated that some of the test samples were below detection level or had very low toxicities. These were then exposed to the freeze-concentration technique in an attempt to increase their toxicities to a range where reliable results could be obtained. The samples so treated included the two taken from the North Saskatchewan River, the oldest sample from within the landfill (#113), and the one closest to the active face (#1 North).

4. RESULTS AND DISCUSSION

The nature of the Clover Bar leachate has changed considerably in the past few years. In a previous study carried out on the same leachate in 1981 (Baker et al. 1981), the strength of the leachates was much higher. **Table 1**, taken from the findings of that study, indicated leachates with very high TOC and COD levels. In comparison, the leachates sampled in the present study were characterized by substantially lower TOC values. This could be taken as a confirmation of continuing degradation processes occurring in the landfill that might ultimately result in leachates with virtually no organic constituents.

The Clover Bar leachates sampled in 1984 had TOC levels in the range of 139 to 815 mg/L, whereas in the earlier study (Baker et al. 1981), the range was 300 to 16 100 mg/L. For example, a comparison of the previous and present results obtained for the same sample site (Samples #2 and #116 in 1981 and 1984 respectively) indicated a decrease of 10 376 mg/L in the TOC level. This well was located in one of the oldest parts of the landfill, and it is possible that degradation processes have reduced the strength of the leachates to a low level. Further, poor hydraulic connection in the wells, probably due to chemical and bacterial action around the well screens, might have affected sample chemistry.

The initial assessment of Clover Bar leachates was made by determining the level of organic constituents using a Dohrmann DC-80 Total Carbon Analyser. The results obtained with this instrument for the eight leachates studied are reported in **Table 2**. The volatiles that constitute an integral part of the organic content of the leachates were low molecular weight organic compounds.

Samples #116, #113, and #1 North represented leachates from the main part of the landfill, and were all within the berm that surrounds the area. These had the highest levels of organic carbon. Samples #101A, #103, and #201 were from wells outside the berm that could represent possible leakage of leachate from the landfill site. These samples indicated lower levels of TOC than those within the berm. The two river samples, taken from above and below the landfill, were collected to determine whether any changes in toxicity could be observed as a result of the river flowing past

Table 1. Organic constituents of Clover Bar leachates, 1981.[a]

Sample	Total Organic Carbon (mg/L)	Chemical Oxygen Demand (mg/L)
#1	1 500	5 100
#2	11 000	25 900
#3	460	430
#4	300	290
#5	1 050	
#6	16 100	29 800
#7	7 200	18 400

[a] From Baker et al. 1981 (see Figure 1).

Table 2. Organic carbon in leachate and river samples*, 1984.

Sample	Total Carbon (ppm)	Volatiles (ppm)	Total Organic Carbon (ppm)	Total Inorganic Carbon (ppm)
Upstream River	25.8	0.8	1.4	23.6
Downstream River	27.6	2.0	1.6	24.0
#113	262	18.0	34.7	209
#116	624	127	225	272
#1 North	815	25	271	519
#101A	139	8.0	24.4	137
#103	146	32	7.5	107
#201	174	24	4.6	145

* Single samples

the landfill. The downstream river sample had a slightly higher TOC than the upstream river sample (Table 2). In all samples, the inorganic carbon was the dominant form of carbon measured. Sample site #1 North was located near the active face of the landfill and showed rapidly growing levels of organic material in leachates samples.

The toxicity of each of the samples, including their toxicities in toxic units, was measured using the Microtox method and is reported in Table 3. This was done because the Microtox procedure generated values in a reverse order. Samples with high toxicity had low EC levels, while low toxicity samples had high EC values. Toxic unit values were determined by dividing 100 by the EC value for the sample in question. The significance of this measurement is demonstrated later during the discussion of the contribution of individual fractions and their toxicities.

The river sample taken upstream of the landfill registered no measurable toxicity (Table 3). However, the downstream river sample depicted finite toxicity levels of 49.5% at 5 min and 44.7% at 15 min. These percentages indicated the EC at which 50% of the luminescent bacteria were destroyed. The recorded differences at the indicated time period were due to individual organic substances having different rates of interaction with the bacteria. Some compounds required a longer time for the same effect on the bacteria and hence showed greater toxicity levels at the end of the longer time period. The converse was noted for leachate sample #116, where greater toxicity was recorded at the 5 min interval than at the 15 min reading. In general, these samples had relatively low levels of toxicity. As would be expected, the samples inside the berm, #113, #116, and #1 North, had the highest toxicities, while the samples representing leachate escaping from the landfill, #101A, #103, and #201, had high EC_{50} values that indicated a lower toxicity.

Analyses of the river samples showed that the river water was influenced by leachate flowing from the landfill; this was depicted by increased toxicity levels in the downstream sample that were similar to those of leachates escaping from the landfill.

There might be some shortcomings in the location selected for the downstream sample. The site selected was about 100 m downstream of the

Table 3. Microtox EC_{50} (5), EC_{50} (15), and equivalent toxic units of leachate and river samples, 1984.

Sample	Toxicities (%)		Toxic Units	
	$EC_{50}(5)$	$EC_{50}(15)$	$\frac{100}{EC_{50}(5)}$	$\frac{100}{EC_{50}(15)}$
Original Samples				
Upstream River	BDL	BDL		
Downstream River	49.5	44.7	2.02	2.24
#113	13.4	13.1	7.46	7.63
#116	9.8	11.9	10.20	8.40
#1 North	45.0	45.7	2.22	2.19
#101A	54.1	26.3	1.85	3.80
#103	43.4	44.8	2.30	2.23
#201	63.1	62.2	1.58	1.61
Concentrated Samples				
Upstream River	221.7	89.1	0.45	1.12
Downstream River	290.4	143.0	0.34	0.70
#113	118.0	104.7	0.85	0.96
#1 North	32.5	27.6	3.08	3.62

EC - Effective Concentration

BDL - Below Detection Limit

eastern limit of the landfill site and 1 m from the river bank. Leachates seeping from the landfill site and intercepting groundwater discharge might have bypassed this specific location. Longitudinal dispersion from a point farther out into the main stream of the river would permit this to occur, and the site chosen would therefore not reflect such inputs.

Although the two river samples depicted lower levels of toxicity, it would have been beneficial to determine contributions to that toxicity by individual classes of compounds in the samples; however, this was not possible. To resolve this dilemma, a technique of freeze concentrating was undertaken. This method was applied not only to the river samples, but also to two other samples with high toxic levels (Table 4). The additional samples were used to verify the accuracy of the freeze-concentrating procedure. As an initial measurement of concentration factor for the samples, TOC levels were recorded for the concentrate itself and for the ice that was frozen out of the samples. Theoretically, there should be no TOC in the ice, and an increased level should be seen in the concentrate equal to the concentration factor due to the freeze-concentrating process. Table 4 outlines the findings of the freeze-concentrating method. Based on values reported for TOC, the process yielded results that were close to the theoretical final values in two of the four samples: the downstream river sample and sample #113. In the other two, the TOC measurements were considerably higher than the theoretically anticipated results. The reason for these increases were not immediately obvious. The results, however, led one to believe that this was a viable process for treating low-level toxic samples, and one that could be expected to provide the concentration required to bring about more reliable toxicity measurements.

Results obtained from the Microtox test using concentrated samples are expressed at the bottom of Table 3. The upstream river sample and #1 North showed increases in toxicity. These were also the samples that indicated a normal increase in TOC values. In contrast, the other two samples, the downstream river and #113, showed significantly reduced toxicities. It is evident that some complex change may have taken place during the course of the freeze-concentration process that may have influenced the character of the original samples. It would appear that

Table 4. Freeze concentration effect on TOC values.

Sample	Original TOC (ppm)	Final Volume Concentrate (mL)	Final TOC (ppm)	Theoretical TOC (ppm)	Comment
Upstream River	2.2	100	27.1	11.2	High
Downstream River	3.6	70	25.8	25.8	Excellent
#113	53.0	100	265	247	Excellent
#1 North	296	220	673	514	High

those samples that experienced a greater-than-expected increase in TOC also were similarly influenced, resulting in greater toxicity. In contrast, two of the samples experienced just the opposite effect regarding reduced toxic levels.

The freeze-concentration method was a relatively new technique and, to the author's knowledge, had not been applied to this kind of system before. While it was theoretically possible that the desired results would be obtained, this study indicated that such was not the case. Instead, a more detailed study should be conducted before this technique can be used effectively to assist in determining results for low-toxicity samples.

One of the original objectives of this study was to attempt to learn what contributions were made to these toxicities by some of the different classes of organic compounds contained in the leachate and water samples. The ion-exchange technique described earlier was applied to each of the eight samples (four original samples and four concentrates). In each case, four fractions were obtained representing phenols, organic acids, organic bases, and organic neutral compounds. Each of the fractions was tested using the Microtox procedure. The results of those measurements are reported in Table 5. No values were obtained for the organic bases because they were all below detection limits. Phenols, very often considered contributors to toxic conditions, were not detected in the river sample taken upstream of the landfill site, but instead small increases were recorded in the river sample downstream of the site. The values of 84.6% in the 5 min reading and 49.2% at 15 min indicated a difference in the phenolic constituents contributing to the overall toxicity of phenols in the sample. This occurred because different members of a class of organic compounds would cause different responses by the luminescent bacteria with time. Phenol is an example of one such toxicant that causes an immediate light loss followed by a period of either slight recovery or stable light output. For other phenols, the light output of the bacteria was still decreasing rapidly at 5 min; therefore, more reproducible results were obtained when 15 min data were used.

Table 5. Microtox EC_{50} (5), EC_{50} (15), and equivalent toxic units on separated fractions of samples.

Sample	Fraction	Toxicities (%) $EC_{50}(5)$	Toxicities (%) $EC_{50}(15)$	Toxic Units $\frac{100}{EC_{50}(5)}$	Toxic Units $\frac{100}{EC_{50}(15)}$
Upstream River	Phenols	BDL[a]	BDL		
	Acids	Interference			
	Neutrals	38.0	24.4	2.63	4.10
Downstream River	Phenols	84.6	49.2	ND[b]	2.03
	Acids	Interference			
	Neutrals	6.25	28.4	1.60	3.52
#113	Phenols	104.8	66.2	0.95	1.51
	Acids	269.7	136.4	0.37	0.73
	Neutrals	75.9	39.5	1.32	2.53
#116	Phenols	BDL	BDL		
	Acids	166.6	129.2	0.60	0.77
	Neutrals	73.6	56.0	1.36	1.79
#1 North	Phenols	107.7	129.5	0.93	0.77
	Acids	303.0	225.9	0.33	0.44
	Neutrals	52.8	36.4	1.89	2.75
#101A	Phenols	BDL	BDL		
	Acids	147.8	86.1	0.68	1.16
	Neutrals	52.6	32.7	1.90	3.06
#103	Phenols	71.8	80.9	1.39	1.24
	Acids	89.5	32.1	1.12	3.12
	Neutrals	123.7	70.3	0.81	1.42
#201	Phenols	BDL	BDL		
	Acids	239.1	223.6	0.42	0.45
	Neutrals	63.7	33.2	1.57	3.01

[a]BDL - Below Detection Limit

[b]ND - No Data

Samples of the phenolic fraction of leachates taken from within the limits of the landfill (inside the berm) indicated very low toxicities: 105% in #113, 108% in #1 North, and below detection in #116. Samples from outside the berm and the landfill area were characterized by similar phenolic toxicities. However, sample #103, located near the active face of the landfill, might have indicated higher levels for phenolic compounds than the outside samples if any leakage from the site had occurred. This was observed with the 5 min toxicity value at 72% and the 15 min toxicity value of 81%. In these cases the phenolic compounds contributing to the toxicity in the sample might have been different from those contributing to the phenolics in the downstream river sample where the 15 min toxicity values were higher (as indicated by a lower percentage) than the 5 min values. This might be better understood by observing the data for the number of toxic units represented by the EC values. (The number of toxic units is determined by dividing 100 by the EC value.) Since the EC_{50} values indicated levels of toxicity in a reverse manner, this procedure would convert all values into a readily understandable orientation. In the toxicity of phenolic compounds in sample #103, the toxic unit values at 5 min and 15 min showed that more toxic units were observed at the shorter time period than at 15 min (1.39 at 5 min as compared with 1.24 at 15 min).

One class of compounds that contributed greatly to the TOC levels in the previous Clover Bar leachates study (Baker et al. 1981) were the organic acids. In sample #6 (#116 in 1984), where the TOC was 11 000 mg/L, the non-volatile organic acids were present at a level of 3000 mg/L. The volatile organic acids, however, were not measured. In the 1984 study the toxicity due to organic acids was consistently low. The river samples contained substances that interfered with toxic measurements, therefore no reliable data were obtained. This kind of interference, thought to be due to the presence of certain metals, resulted in an increase in light output rather than the expected decrease due to the presence of toxic species. The leachates from wells #116, #113, and #1 North had very low toxicities, with EC_{50} values of between 150% and 300%, or substantially less than one toxic unit. The wells outside the site were characterized by similar toxic levels. Once again, well #103 showed EC_{50} values for organic acids at 90%, low but finite, because

the more slowly responding organic acids appeared in this sample where EC_{50} values indicated a higher toxicity at 15 min than at 5 min.

Of the four fractions obtained by the ion exchange separation procedure, the one containing the neutral compounds contributed most to the toxicity of the samples. The two river sites depicted interesting toxicity levels in which the downstream sample had a lower neutral toxicity than the upstream sample. This could be due to the fact that when all organic compounds were together in a "whole" sample, either synergistic or antagonistic toxic effects might have occurred. The exact nature of these interactions is not well known. It would appear that in the samples being investigated in this study, the toxicity of separated neutral compounds was enhanced following separation. In none of the samples was the toxicity abnormally high, but the neutral compounds represented the most toxic fraction in the total sample. In the three samples from within the bermed area of the landfill, toxicities at 5 min ranged from 53% to 75%. At 15 min they were higher, between 35% and 56%; this again indicated the presence of toxic constituents that took longer to bring about their total influence on the bacteria. Toxicities of samples immediately outside the landfill were characterized by slightly lower values ranging between 53% and 125% at 5 min and 33% to 70% at 15 min.

The overall concept of toxicity is more clearly understood if the EC values reported for each fraction and samples are expressed in terms of toxic units. This form of reporting is included in Table 5 along with the regular EC_{50} data. While the use of toxic units is a convenient method for comparing toxicities, it does not directly indicate the ability of the sample under investigation to influence the light-emitting bacteria. The definition of the EC_{50} is the percentage concentration of the sample solution that will reduce the light output of the bacteria by 50%. If a value in excess of 100% is obtained, the reading implies that the solution requires concentration to reduce the light output by 50%. In contrast, the number of toxic units portrayed by that EC_{50} is only a mathematical expression that is convenient for comparing toxicities.

An attempt was made to compare total toxicities of the four fractions with the toxicity of the original sample, whether the original sample was "as received" or a concentrated one obtained by freeze concentration. The comparisons are reported in Table 6. In general, the sum of toxicities of the individual fractions was not fully equal to the toxicity of the whole sample. This could only be accounted for by realizing that in the whole sample, synergistic effects might have occurred tnat could have enhanced the individual toxicities. In some cases, the opposite effect (antagonism) was noted, but the majority of samples indicated synergism. The antagonistic effect was observed in the two samples representing the oldest part of the landfill, #113, and #116. In all other samples, including the river samples, synergistic effects were observed. Despite these synergistic or antagonistic effects, the most toxic readings were noted in samples taken from within the landfill site, intermediate values were noted in sample immediately outside the berm, and the lowest values were noted in the North Saskatchewan River samples.

Table 6. Toxicity material balances.

Sample	$\frac{100}{EC_{50}(5)}$		$\frac{100}{EC_{50}(15)}$	
	Whole	Fraction Total	Whole	Fraction Total
Upstream River		2.63		4.10
Downstream River	2.02	2.98	2.24	3.52
#113	7.46	2.64	7.63	4.77
#116	10.20	1.96	8.40	2.56
#1 North	2.22	3.15	2.19	3.96
#101A	1.85	2.58	3.80	4.22
#103	2.30	3.32	2.23	5.78
#201	1.58	1.99	1.61	3.46

5. SUMMARY AND CONCLUSIONS

Samples for toxicity analyses were obtained from three locations within the Clover Bar Landfill near Edmonton, Alberta, from three wells immediately outside the landfill site (between the site and the adjacent North Saskatchewan River), and from the North Saskatchewan River (one river sample from a location immediately above the site and one immediately below). The latter two were taken to determine any change in toxicity that could be directly attributed to the Clover Bar Landfill operation. The samples were immediately placed in ice-cooled chests, transported to the laboratory, and stored in a refrigerator until ready for analyses. Initial organic carbon measurements were taken so that comparisons could be made with the strength of leachates sampled in a previous study (Baker et al. 1981). The 1984 sampling indicated a significant decrease in leachate strength. The TOC for one specific sample taken in 1981 was 11 000 mg/L, while that for a sample taken in 1984 at the same location was 225 mg/L. This reduction in strength immediately indicated the probability of considerably decreased toxicities and the concomitant decrease in external effects due to leachate toxicity.

Measurements made using the Microtox method confirmed relatively low toxicities for all eight samples. Samples from inside the landfill site had the highest levels, followed by those immediately outside the site, with the river samples having the lowest levels. The upstream river sample toxicity was below detection limits. Four of the collected samples were used for a freeze-concentration technique in an attempt to enhance toxicities to obtain more meaningful and reliable results. TOC levels were increased according to the degree of concentration. Toxicity measurements were not as reliably altered. Two samples, the upstream river sample and the other from near the active operating face of the landfill, were significantly enhanced, while two others representing the downstream river sample and one from the oldest areas of the landfill showed a reduction in toxicity. The four concentrated samples, as well as the remaining original samples, were subjected to the ion exchange procedure for separating each sample into phenols, organic acids, organic bases, and neutral compounds. Microtox measurements of these fractions indicated no toxicity due to organic bases, slight toxicity due to organic acids, a random slight toxicity contributed by phenols, and the

majority of toxicity due to neutral compounds. Conversion of EC toxicities to toxic units showed that the toxicity of each whole sample was not equalto the sum of toxicities due to the individual contributing classes of organic compounds. This might have occurred as a result of synergistic or antagonistic effects when the fractions were associated with each other in the whole sample. In the majority of samples and their concomitant fractions, synergism appeared to be the more common effect.

It might be concluded that the toxicity of leachates from the old part of the Clover Bar landfill has probably decreased over the past several years to the point that the site would not create a situation requiring additional monitoring or remedial action.

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